DEVELOPMENT OF CATALYSTS FOR THE HYDROCRACKING OF POLYNUCLEAR AROMATIC HYDROCARBONS

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INTRODUCTION

Hydrocracking reactions of polynuclear aromatic hydrocarbons and heterocyclic compounds proceed essentially through a multi-step mechanism of hydrogenation, isomerization, cracking and rehydrogenation in that order. Multi-functional catalysts containing hydrogenation, isomerization and cracking activities will thus be the most suitable catalysts for reactions of this type. Cracking catalysts like the silica-aluminas and molecular sieves and hydrogenation catalysts like metallic platinum, palladium, nickel and oxides and sulfides of cobalt, molybdenum, nickel and tungsten were used in suitable combinations in the preparation of multi-functional catalysts used in the industrial processing of petroleum feed stocks (1-3). The industrial catalysts may not be quite suitable for use in the processing of highly aromatic feed stocks like the coal oils and their activities and selectivities may have to be modified to make them suitable for use. Not much work was published in the open literature on the activities and selectivities of different catalysts in the hydrocracking of polynuclear aromatic hydrocarbons. Flin et al (4) and Sullivan et al (5) studied the hydrocracking of different aromatic hydrocarbons over catalysts containing nickel sulfide on silica-alumina in flow systems. The principal reactions occured during hydrocracking were found to be hydrogenation, cracking, isomerization, alkylation and paring. Qader and Hill (6) later reported product distributions obtained in the hydrocracking of naphthalene and anthracene over dual functional catalysts containing oxides of cobalt, molybdenum, nickel and silica-alumina. In the present communication, the data on the kinetics and mechanisms of hydrocracking of naphthalene, anthracene and pyrene are reported. The activities and selectivities of oxides and sulfides of cobalt, molybdenum, nickel and tungsten and different cracking catalysts are also discussed.

EXPERIMENTAL

Pure grade hydrocarbons and catalysts were used. The catalysts contained 20 and 80 per cent by weight of hydrogenation and cracking catalysts respectively. The hydrocracking work was done in a stirred tank reactor of 300 c.c. capacity. Experiments were done with 10 gm of the hydrocarbon and 2.5 gm. of the catalysts in the temperature range of 450° - 500°C and pressure of 500 - 1250 psi.

RESULTS AND DISCUSSION

Coal oils contain large quantities of polynuclear aromatic hydro-carbons and heterocyclic compounds. An understanding of the conversion

of polynuclear structures to smaller molecules will help in developing efficient processes for the conversion of coal oils. Hydrocracking is a versatile method for the conversion of higher aromatics to lower ones and catalysts containing hydrogenation and cracking activities will be the most suitable for this reaction. In this work, Naphthelene was hydrocracked over catalysts containing prereduced oxides and sulfides of Mo, Ni, Co and W and silica-alumina. The product distributions obtained with the oxide catalysts are given in Tables I and II. The principal products of naphthalene hydrocracking are Tetralin, indanes, ethylbenzene, toluene and benzene (Table I). At higher conversion levels (Table II), butyl benzenes and compounds boiling higher than naphthalene were also formed. The higher compounds were found to be mainly alkyl naphthalenes and Tetralins. Similar product distributions were obtained when naphthalene was hydrocracked over sulfide catalysts as shown in Tables III and IV. The data show that the oxide and sulfide catalysts affect the hydrocracking reaction in a similar way. The product distribution data obtained with different cracking catalysts and molybdenum oxide are given in Table V. The data show that the catalysts have different activities but yield similar products. It is, therefore, evident that the hydrocracking pattern of naphthalene remains same irrespective of the catalyst used. The catalysts, however, vary in their activities and selectivities. The product distribution data of naphthalene hydrocracking suggest a three step reaction mechanism as shown in Figure 1. In the first step, naphthalene gets hydrogenated to Tetralin which then gets isomerized in a second step to methylindan. Methylindan will then crack in a third step to indan and alkylbenzenes. The indan further cracks to alkylbenzenes. The analysis of the gaseous products given in Table VI also supports the mechanism given in Figure 1. A similar mechanism was earlier proposed by Qader et al (7) in the hydrocracking of naphthalene over a H-mordenite catalyst. The kinetics of each individual step of the naphthalene hydrocracking reaction were evaluated in the temperature range of 450° - 500°C at a constant hydrogen pressure of 1000 psi. All the steps were found to be first order reactions with respect to the concentration of naphthalene and the activation energies were calculated from plots of Arrhenius equation. The rate constants of the hydrogenation, isomerization and cracking reactions were found to be consistent with equations 1 - 3.

$$k_{Hydrogenation}: \quad 1 \times 10 \; e^{-8,600/RT} \; min.^{-1} \qquad (1)$$

$$k_{Isomerization}: \quad 1 \times 10^{1.6} e^{-18,400/RT} \; min^{-1} \qquad (2)$$

$$k_{Cracking}: \quad 1 \times 10^{3.8} e^{-28,100/RT} \; min^{-1} \qquad (3)$$

The activation energies indicate that hydrogenation is controlled by both physical and chemical processes, isomerization and cracking mainly by chemical reaction. The effect of hydrogen pressure on the first order rate constants is shown in Figure 2. The rate constants

increased almost linearly with pressure. The hydrogenation rate
constant increased relatively more when compared to the isomerization
rate constant which increased more than the cracking constant. The
data indicate that the overall order of the reaction is more than
one, being greater than zero with respect to hydrogen concentration
and the rates are influenced to different degrees by physical and
chemical processes.

The product distributions of anthracene hydrocracking are given
in Tables VII-IX. The main products obtained were hydrogenated anthracenes,
hydroanthracene isomers containing 5 member saturated rings of the
acenaphthene type, naphthalenes, Tetralins and alkylbenzenes. Some
compounds higher than anthracene were also formed. The hydrocracking
pattern was found to be the same irrespective of the catalyst type
used. The hydrocracking rate, however, varied with the catalyst type.

The product distribution data suggest a multi-step reaction mechanism
occuring in the hydrocracking of anthracene as shown in Figure 1.

The principal reactions occuring during anthracene hydrocracking
are hydrogenation, skeletal isomerization and cracking. The hydrogenation
of anthracene was earlier reported (8) to take place in a stepwise manner
forming di-, tetra- and octahydroanthracenes in that order. But at high
temperatures, the dihydroanthracene did not form to any significant
extent. Under the conditions (450° - 500°C) used in this work, dihydro-
anthracene did not appear in the product to any significant extent.
No isomerization of the hydroanthracenes to acenaphthene type structures
was reported in the above work (8). However, Sullivan et al (5) reported
the formation of isomeric hydrophenanthrenes containing 5-member saturated
rings in the hydrocracking of phenanthrene. In this work, the isomeric
hydroanthracenes containing 5-member saturated rings were formed as shown
in Figure 1. Though compounds containing one 5-member ring are shown
in the mechanism, it is possible that compounds containing two 5-member
rings might form from octahydroanthracene. The naphthalenes and Tetralines
will undergo hydrocracking according to the mechanism shown in Figure 1.
The kinetics of the overall hydrogenation and cracking steps of the
anthracene hydrocracking reaction were evaluated in the temperature range
of 450° - 500°C at a constant pressure of 1000 psi. Both the steps were
found to be first order reactions with respect to the concentration of
anthracene and the activation energies were calculated from plots of
Arrhenius equation. The rate constants were found to be represented by
equations 4 and 5 in the temperature range 450° - 500°C.

$$k_{Hydrogenation}: \quad 1 \times 10^{1.2} e^{-11,100/RT} \ min^{-1} \quad\quad (4)$$

$$k_{Cracking}: \quad 1 \times 10^{0.2} e^{-16,200/RT} \ min^{-1} \quad\quad (5)$$

The activation energies indicate that hydrogenation and cracking are
mainly controlled by chemical processes. The effect of hydrogen pressure
on the first order rate constants is shown in Figure 3. The rate constants
increased linearly with pressure. The relative increase in the rate

constants was large in case of hydrogenation when compared to cracking.
The data indicate that the reactions are controlled by chemical processes
to different degrees The mechanism of anthracene hydrocracking remained
same irrespective of the catalyst used. However, the rates of hydro-
cracking varied with the catalyst type. The data given in Table X show
that cobalt sulfide is the most active hydrogenation catalyst followed
by tungsten sulfide, nickel sulfide and molybdenum sulfide in that order.
The hydrocracking activities also decreased in the same order though
the same cracking catalyst is used. This indicates that cracking increases
with hydrogenation probably due to the increased formation of hydroanthracenes.
It, therefore, appears that a more active hydrogenation catalyst also
enhances cracking reactions indirectly. The hydrogenation and cracking
rate constants of anthracene also varied with the type of cracking catalyst
used as shown in Table XI. The low alumina catalyst exhibited higher
cracking activity. The hydrogenation rate constant was also high in
case of the low alumina catalyst though the same hydrogenation catalyst
is used in both the cases. This indicates that cracking increases hydro-
genation indirectly.

The product distribution data of pyrene hydrocracking (Table XII
and XIII) indicate that the oxide and sulfide catalysts yield similar
product distributions. The hydrocracking reaction proceeds through
a multi-step mechanism of hydrogenation, isomerization and cracking.
The pyrene gets converted to phenanthrenes through a two step mechanism
of hydrogenation and cracking. Then the phenanthrenes formed get con-
verted to naphthalenes which in turn get converted to alkylbenzenes. The
principal steps involved in the conversion of pyrene to benzenes are
shown in Figure 1. The pyrene hydrocracking data were evaluated by first
order kinetics and the first order rate constants were found to be
represented by equations 6 and 7:

$$k_{Hydrogenation}: \quad 1 \times 10^{2.1} e^{-7,100/RT} min^{-1} \quad (6)$$

$$k_{Cracking}: \quad 1 \times 10^{0.6} e^{-10,200/RT} min^{-1} \quad (7)$$

The activation energies indicate that hydrogenation is controlled by
both physical and chemical processes and cracking by chemical reaction.

The reactivities of the different polynuclear aromatic hydrocarbons
vary due to differences in their chemical, physical and electronic
properties. The first order rate constants of the hydrocarbons given
in Table XIV indicate that anthracene is the most reactive hydrocarbon
and naphthalene the least reactive.

ACKNOWLEDGMENT

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TABLE I.   NAPHTHALENE HYDROCRACKING

Cracking Catalyst: Silica-(High) Alumina

Hydrogenation Catalyst:	Mo O_3	N10	Co O	WO_3
Liquid Product Analysis, Mole %				
Benzene	0.75	0.69	0.97	Trace
Toluene	0.75	1.39	1.30	Trace
Ethyl benzene	0.5	Trace	0.65	0.27
Xylenes	-	-	-	-
Propyl benzenes	-	-	-	-
Decalins	-	-	-	-
Butyl benzenes	Traces	-	-	Traces
Indan	1.6	0.5	1.2	1.09
Methyl Indan	3.42	2.28	3.68	3.0
Tetralin	5.02	2.78	4.88	2.73
Naphthalene	87.93	90.59	84.69	92.89
Higher Compounds	Traces	1.74	2.6	-

TABLE II.   NAPHTHALENE HYDROCRACKING

Cracking Catalyst: Silica-(High) Alumina

Hydrogenation Catalyst:	Mo O_3	N10	Co O	WO_3
Liquid Product Analysis, Mole %				
Benzene	0.63	1.7	0.37	0.47
Toluene	1.19	3.1	0.79	1.25
Ethyl benzene	2.54	5.5	3.47	0.78
Xylenes	-	-	-	-
Propyl benzenes	0.63	0.56	Trace	Trace
Decalins	Trace	0.9	Trace	Trace
Butyl benzenes	5.09	4.9	4.17	1.41
Indan	3.45	4.0	2.46	1.72
Methyl Indan	6.1	5.11	4.0	3.0
Tetralin	35.66	27.9	37.26	22.04
Naphthalene	38.85	41.37	41.25	60.62
Higher Compounds	5.09	4.9	5.98	8.66

TABLE III. NAPHTHALENE HYDROCRACKING

Cracking Catalyst: Silica-(High) Alumina

Hydrogenation Catalyst:	MoS_2	NIS	Cos	WS_2
Liquid Product Analysis, Mole %				
Benzene	3.8	1.49	Trace	1.34
Toluene	3.04	1.49	Trace	1.67
Ethyl Benzene	1.90	1.49	Trace	0.67
Xylenes	-	-	-	-
Propyl benzenes	-	-	-	- -
Decalins	-	-	-	-
Butyl benzenes	Trace	Trace	-	Trace
Indan	2.74	1.30	1.5	1.70
Methyl Indan	6.0	3.17	2.94	5.01
Tetralin	8.36	4.47	3.11	6.71
Naphthalene	74.14	85.56	92.44	81.85
Higher Compounds	Traces	Traces	Traces	4.02

TABLE IV. NAPHTHALENE HYDROCRACKING

Cracking Catalyst: Silica-(High) Alumina

Hydrogenation Catalyst	MoS_2	NIS	Cos	WS_2
Liquid Product Analysis, Mole %				
Benzene	0.16	0.44	Trace	Trace
Toluene	0.48	1.17	0.52	0.47
Ethylbenzene	0.8	0.88	0.87	0.94
Xylenes	-	-	-	-
Propylbenzenes	-	-	-	-
Decalins	-	-	-	-
Butylbenzenes	1.61	2.2	1.05	2.36
Indan	0.8	2.1	1.02	1.30
Methyl Indan	1.61	6.0	1.6	2.17
Tetralin	28.98	25.32	21.89	29.69
Naphthalene	61.85	55.22	66.9	58.45
Higher Compounds	3.7	6.62	6.12	4.58

TABLE V.   NAPHTHALENE HYDROCRACKING

Hydrogenation Catalyst: Reduced Mo O_3

Cracking Catalyst:	SiO_2-(High) Al_2O_3	SiO_2-(Low) Al_2O_3	XZ-36	H-Zeolon
Liquid Product Analysis, Mole %				
Benzene	0.66	6.15	8.86	11.94
Toluene	3.34	6.15	6.66	5.11
Ethylbenzene	3.78	5.64	3.33	2.73
Xylenes	-	-	-	-
Propylbenzenes	-	Traces	-	-
Decalins	-	Traces	-	-
Butylbenzene	4.45	4.61	2.22	1.7
Indan	1.58	6.23	7.32	3.41
Methyl Indan	5.10	12.23	9.34	13.65
Tetralin	34.52	17.94	20.00	23.89
Naphthalene	44.54	35.68	33.33	32.42
Higher Compounds	2.0	5.33	8.88	5.11

TABLE VI.   NAPHTHALENE HYDROCRACKING

PRODUCT NUMBER:	1	2	3	4
Analysis, Vol. %				
Methane	Nil	Trace	6.2	13.6
Ethane	Trace	4.25	15.6	16.6
Propane	100	95.75	78.1	62.5
Butane	Trace	Trace	Trace	8.3

TABLE VII.   ANTHRACENE HYDROCRACKING

Cracking Catalyst: Silica-(High) Alumina

Hydrogenation Catalyst:	Mo O_3	NIO	Co O
Composition of Liquid Product, Mole %			
Anthracene	4.46	5.57	5.9
Tetrahydroanthracene	20.6	25.80	19.5
Octahydroanthracene	13.9	8.62	8.2
Hydroanthracene isomers	3.2	2.80	3.27
Naphthalenes	41.95	43.14	44.1
Benzenes	13.50	13.20	18.5

TABLE VIII.   ANTHRACENE HYDROCRACKING

Cracking Catalyst: Silica-(High) Alumina

Hydrogenation Catalyst:	Mo S_2	NIS	Cos	WS_2
Composition of Liquid Product, Mole %				
Higher Boiling Compounds (Unidentified)	3.69	5.15	6.66	2.51
Anthracene	32.28	23.71	20.0	22.61
Tetrahydroanthracene	6.45	4.63	2.85	5.40
Octahydroanthracene	13.83	15.86	14.27	14.56
Hydroanthracene Isomers	1.10	2.87	3.80	5.01
Naphthalenes	37.24	40.17	43.21	41.04
Benzenes	4.54	7.52	9.13	8.77

TABLE IX.   ANTHRACENE HYDROCRACKING

Hydrogenation Catalyst: MoS_2

Cracking Catalyst:	Silica-(High) Alumina	Silica-(Low) Alumina	H-Zeolon
Composition of Liquid Product, Mole %			
High Boiling Components (unidentified)	3.69	6.11	0.85
Anthracene	32.28	22.77	19.17
Tetrahydroanthracene	6.45	3.88	21.92
Octahydroanthracene	13.83	16.66	27.50
Hydroanthracene isomers	1.10	6.32	9.1
Naphthalenes	37.24	35.42	16.30
Benzenes	5.34	8.76	5.05

TABLE X.   RATE CONSTANTS OF ANTHRACENE

Temp: 450°C   Press: 1000 psi
Cracking Catalyst: Silica-(High) Alumina

Hydrogenation Catalyst	$k_{Hydrogenation} \times 10^4$	$k_{Hydrocracking} \times 10^4$
CoS	650	268
MoS_2	510	136
NiS	590	206
WS_2	600	263

TABLE XI. RATE CONSTANTS OF ANTHRACENE

Temp: 475°C, Press: 1000 psi

Hydrogenation Catalyst: MoS_2

	$k_{Hydrogenation} \times 10^4$	$k_{Hydrocracking} \times 10^4$
Silica-(High) Alumina	510	136
Silica-(Low) Alumina	610	208

TABLE XII. PYRENE HYDROCRACKING

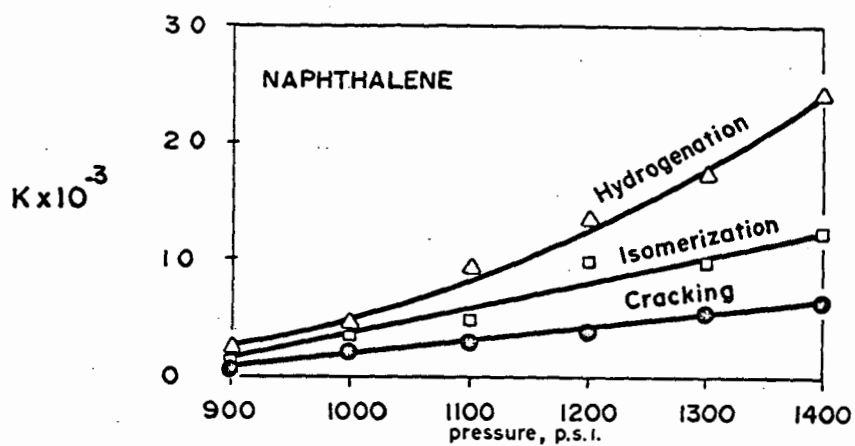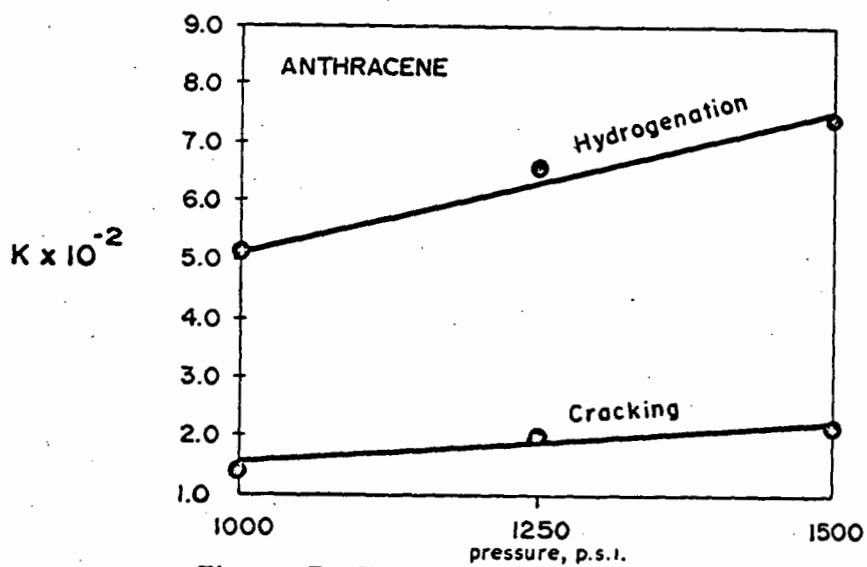| Hydrogenation Catalyst:	Mo O_3	NlO	CoO	WO_3
Liquid Product Composition, Mole %				
Pyrene	67.18	73.72	83.27	71.64
Hydropyrenes	21.09	16.94	13.50	15.5
Phenanthrenes	3.12	1.69	1.35	3.86
Hydro Phenanthrenes	Nil	Nil	Nil	5.97
Hydrophenanthrene Isomers	7.03	4.14	1.5	Nil
Naphthalenes	1.56	3.29	0.37	2.97
Benzenes	Nil	0.16	Nil	Nil

Figure 2. Effect of hydrogen pressure on rate constant

Figure 3. Effect of pressure on rate constant